

## Methane Oxidation in the Open Ocean: Final Report

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**Introduction**

The distribution of methane, its biological consumption in various marine environments, and the impact of this consumption on the air/sea methane flux has been the focus of this project. Measurements of methane concentrations and oxidation rates can provide information on exchange rates between the ocean and atmosphere and can also provide rough limits for the *in situ* methane production rate. Methane is supersaturated in surface seawater and the air/sea methane flux contributes a few percent of the global methane flux. As a product of anaerobic metabolism, the source of methane in anoxic environments is an obvious source of methane to the water column of some environments. However, even in the surface layer of the well oxygenated open ocean environment, methane exhibits a subsurface concentration maximum and surface waters are slightly saturated with respect to the atmosphere. The subsurface maximum that is a ubiquitous feature of oceanic environments was a special focus of this project.

The main goals of this project were to 1) measure methane distributions and oxidation rates in ocean waters and 2) use this information to calculate net consumption terms and estimate fluxes between ocean and atmosphere. During the first two years of this project, we worked in two environments which include deep anoxic layers rich in methane. In the third year, we studied an open ocean environment where deep water and sediments are not possible sources of methane. Results from the completed work are summarized below.

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## Summary of Results

Methane fluxes and methane oxidation in stratified water columns: The first two field sites in which we measured methane distribution and methane oxidation rates were the Cariaco Trench and Saanich Inlet, British Columbia. Both are highly stratified and contain high methane concentrations in anoxic bottom waters. The Cariaco, by virtue of sea floor topography, is stable on a scale of hundreds to thousands of years, and methane concentrations in the anoxic layer have been steadily increasing over time (Scranton, 1988). Saanich Inlet is an intermittently anoxic fjord, and methane accumulates in the deep water over the summer season. Results from both of these environments have been published (Ward et al., 1987, *Nature*; Ward et al., 1988, *Continental Shelf Research*). Additional results from Saanich Inlet are in press (Ward and Kilpatrick, 1990, *Continental Shelf Research*). It seems likely that our results from these two sites can be extended to other similar environments:

- The subsurface methane maximum was not directly related to the anaerobic methane source in deep water and probably derives from horizontal transport of shelf waters or, possibly, *in situ* metabolism by a currently unidentified pathway. This substantiates earlier findings (Scranton and Brewer, 1977; Lilley et al., 1982).
- The surface waters are small sources of methane to the atmosphere.
- Methane oxidation occurs in both oxic and anoxic layers. Highest rates are found at the oxic/anoxic interface region.
- The flux of methane from the deep water to the overlying oxygenated layer is minimized by oxidation at the oxic/anoxic interface region.

In July 1988 we collaborated with other NASA and NSF investigators on an expedition to the Black Sea, where we studied methane and carbon cycling in this stratified environment. My effort focused on methane oxidation in the oxic surface layer and across the oxic/anoxic interface using a  $^{14}\text{CH}_4$  tracer as in the previous field work. Our results from the Black Sea are essentially consistent with those above. Very low rates were detected in the oxic surface water and rates increased to a maximum at the interface, remaining nearly

constant with depth from the interface at about 120 m to the bottom at more than 2000 m. Oxidation rates in the water column suggested a relatively rapid turnover of methane in the anoxic layer, much faster than the water itself is replenished. The striking maximum usually observed at oxic/anoxic boundaries was not found in the Black Sea, perhaps because of the presence of a suboxic layer, rather than a sharp boundary between oxygen and methane bearing waters. A manuscript describing these results is in press in Deep Sea Research (Reeburgh et al., 1990).

Methane fluxes and methane oxidation in oceanic environments: Unlike the stratified environments above, the occurrence of methane in the well oxygenated open ocean has no obvious source. Diffusion from anoxic sediments may explain methane enrichment in nepheloid layers, but cannot easily explain the subsurface methane maximum in near surface waters. Because the ocean covers such a large portion of the earth's surface, however, the production and consumption of methane in these waters could be important on a global scale. We chose the Southern California Bight as a site representative of many deep water oceanic environments. It is moderately oligotrophic, and at our study site, the depth of the water column (900 m) precludes the direct contribution of sediments to surface water chemistry. Oxygen is present all the way to the bottom, although it is depleted in some of the borderland basins and there is evidence of denitrification in the bottom sediments.

Even in this oligotrophic environment, a well defined subsurface methane concentration maximum was detected. Maximum concentration during October 1987 was about 7 nM at a depth of about 80m to 100m. The primary nitrite maximum was slightly shallower, at 65 m. Thus the methane maximum occurred below the bottom of the euphotic zone. Below this depth, methane concentration decreased gradually to less than 1 nM at 850 m. Water column depth was 910 m. We occasionally detected elevated methane concentrations (about 10 nM) a few meters above the sediment/water interface. The gradual decrease in methane concentration with depth was interrupted by a distinct maximum at 500 m (5 nM). This maximum was not correlated with features in oxygen concentration or in nutrient distributions.

Samples for methane oxidation measurements were chosen on the basis of the methane

distribution described above. Time course experiments in the surface layer did not yield linear results. While some activity above zero-time controls was observed at every depth, the data are not robust enough to compute reliable rates from them. This was not the case in deeper water, where, especially around the 500 m concentration maximum, linear oxidation over 24 h was observed.

A second cruise to the Southern California Bight was supported by the National Science Foundation in June 1988. The basic features observed in October, both the methane distribution and the distribution of methane oxidation, were observed again. Methane turnover in the vicinity of the intermediate depth methane concentration maximum was substantially faster than at the subsurface maximum. We suggest this methane (in the 500 meter depth range) is advected into the basins from seeps in the borderland closer to the coast. The coast of California is a known petroliferous area, with many documented seeps in the Los Angeles area, shoreward of our central basin station. Manuscripts reporting on the Southern California Bight work are in preparation and will be forwarded when available.

## **Conclusions**

An important finding from the research described above is that methane oxidation in the marine environment is an important factor in modifying the net flux of methane to the atmosphere. Oxidation ensures that this flux is small, even when the source term in the case of stratified anoxic waters is quite large. This is true for anaerobic methane oxidation in marine sediments and in anoxic waters in stratified water columns, and also for aerobic methane oxidation in oxygenated oceanic environments. Thus, methane is an important, incompletely understood, part of the ocean's carbon cycle, but is itself cycled so efficiently that the ocean is a very small methane source to the atmosphere on a global scale. It seems likely, however, that oxidation modifies not only the amount of methane reaching the atmosphere, but also the isotopic ratio of the methane left behind, or remaining to contribute to the small residual oceanic flux. Controversy currently rages over whether the known sources and sinks for methane are adequate to explain the observed isotopic signature of atmospheric methane. Thus the effect of oxidation by marine bacteria on the isotopic content of methane and its oxidation products may be a small part of this puzzle.

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